THERMOCHEMISTRY

- Thermochemistry is the study of the quantity of heat energy released or absorbed in a chemical reaction.
  Example: the burning of fuel: is a heat-evolving reaction

- Heat : is a form of energy

- Energy: -the potential to do work (to move matter)
  -exists in many different forms:
  - Electrical energy
  - Kinetic Energy (energy of motion)
  - Light energy
  - Heat energy
  - Chemical energy (energy of substances)

- Different forms of energy can be interconverted
  Examples: Light bulb: electrical energy is converted to light energy and heat energy

  Car engine: chemical energy $\longrightarrow$ heat energy $\longrightarrow$ kinetic energy
  (from gasoline)

KINETIC ENERGY (Ek)

- Definition: is the energy associated with a moving object

- Formula: $E_k = \frac{1}{2} mv^2$, where
  m = mass of the moving object (in kg)
  v = speed of the moving object (in m/s)

NOTE: Two objects moving at different speeds may have the same kinetic energy
Example: slow moving truck and fast moving sports' car

SI unit of energy = from formula of energy = **$kg \cdot m^2/s^2$** = **joule (J)**
The **joule (J)** is a very a very small unit

Non-SI unit of heat energy : **The calorie (cal)**
amount of energy required to raise the temperature of one gram of water by one degree Celsius

1 cal = 4.184 J

POTENTIAL ENERGY (Ep)

- Definition: - the energy of an object has because of its position in a field of force
  - is stored energy

- Example: Any object above ground level possesses Potential Energy since it is attracted by the gravitational force. As such, it has the potential to fall, and therefore to move. (Potential Energy changes into Kinetic Energy)

- Formula: **$E_p = mgh$,** where m = mass of the object
  g = constant acceleration of gravity
  h = height (level) of the object aboveground level

NOTE: differences of level are usually more important

As an object falls toward ground level:
- its Ep decreases (h decreases)
- its Ek increases (object speeds up; v increases)

INTERNAL ENERGY (U)

- Definition: the sum of the kinetic and potential energies of the particles making up a substance.

In general: Total Energy of a Substance = **U + Ek + Ep**

NOTE: A substance at rest, in a flask in the laboratory
- possesses no kinetic energy
- potential energy is ignored
- **possesses Internal Energy**

Total Energy of the Substance = Internal Energy of the Substance = U

Conversions of different forms of energy are governed by :

The Law of Conservation of Energy:

- **Energy may be converted from one form to another, but the total quantity of energy remains constant.**

HEAT OF REACTION

- Thermodynamics: is the science of the relationships between heat energy and other forms of energy

  Ek , Ep , U :are thermodynamic properties of matter

- Thermodynamic System: the substance or mixture of substance undergoing a physical or a chemical change
- The Surroundings: everything around the thermodynamic system

Definition of Heat:

- **The energy that flows into, or out of a system because of a difference in temperature between the thermodynamic system and its surroundings.**

This assumes that the system and its surroundings are in thermal contact, (that is, they are not thermally insulated).

Example: hot coffee in a thermos is thermally insulated from its surroundings

Direction of Heat Flow :

- **Heat always flows from a region of higher temperature to a region of lower temperature until the temperatures of the two regions become equal (thermal equilibrium).**

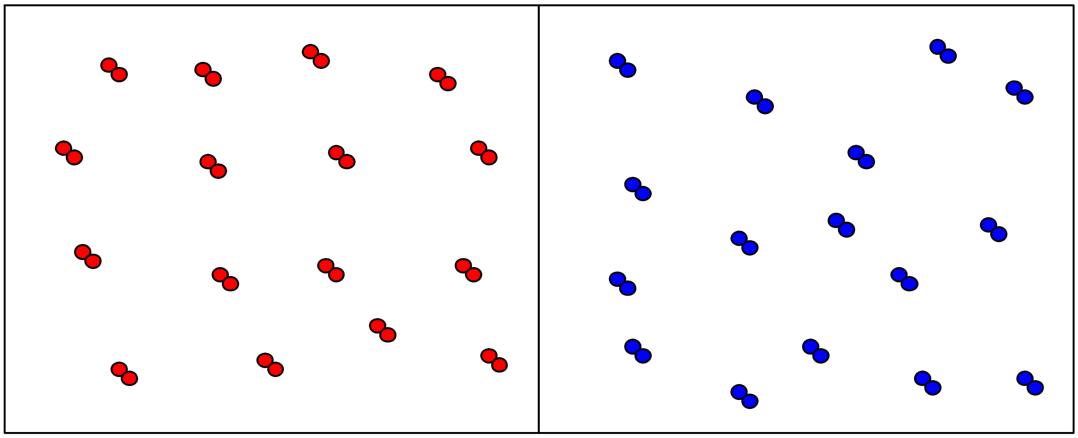
1. If heat energy flows into a system from its surroundings, its internal energy increases:

   Example: A glass of ice water slowly reaches room temperature.
   The internal energy (U) of the water increases, as it warms up.

2. If heat energy flows out from a system into the surroundings, its internal energy decreases

   Example: A cup of hot tea slowly reaches room temperature
   The internal energy (U) of the tea decreases, as it cools down.

EXPLANATION OF HEAT FLOW



HOTTER GAS
FASTER MOVING MOLECULES

COLDER GAS
SLOWER MOVING MOLECULES

Average Molecular Speed of Hotter Gas $>$ **Average Molecular Speed of Colder Gas**

Faster moving molecules slow down

Slower moving molecules speed up

- The Average Molecular Speed in the two containers becomes equal.

- The temperatures of the two gases become equal.

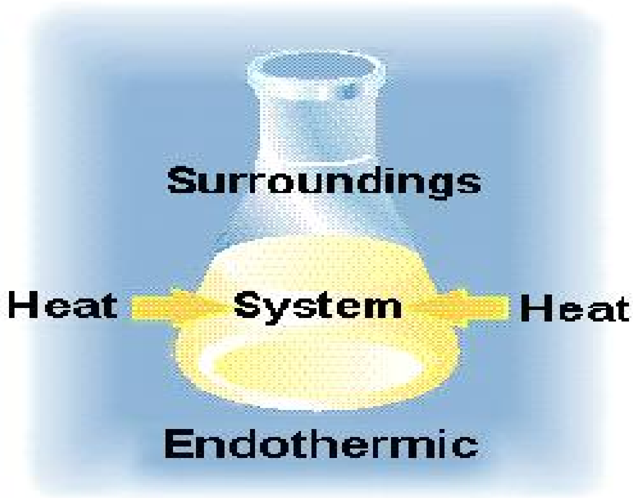
- **A given quantity of heat will raise the temperature of a gas more if the sample is small.**

  Reason: The Absolute Temperature is directly proportional to the Average Kinetic Energy

    - When you add heat to a gas, you increase its total Ek
    - The increase in E_k will be distributed over all the molecules in the sample
    - The increase in average Ek per individual molecule (the increase in temperature) will be greater if there are fewer molecules.

SYMBOL FOR HEAT

- The symbol for heat is q.
- **In a chemical equation, q is always considered a reactant**



heat is absorbed by the system from surroundings

Reactants + q $\longrightarrow$ Products

heat is evolved by the system to the surroundings

Reactants $\longrightarrow$ Products + q

By convention, in a chemical equation q (the Heat term) is always considered a reactant.

Reactants + q $\longrightarrow$ Products

q is positive

- Temperature of the surroundings decreases.
- **Reaction vessel cools**

Reactants - q $\longrightarrow$ Products

q is negative

- Temperature of the surroundings increases.
- **Reaction vessel warms**

<u>Example:</u>
Ammonia burns in the presence of a platinum catalyst to produce nitrogen monoxide.

$$4\ NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$$

In an experiment, 4 mol of NH_3 is burned and evolves 1170 kJ of heat. Is the reaction endothermic or exothermic? What is the value of q?

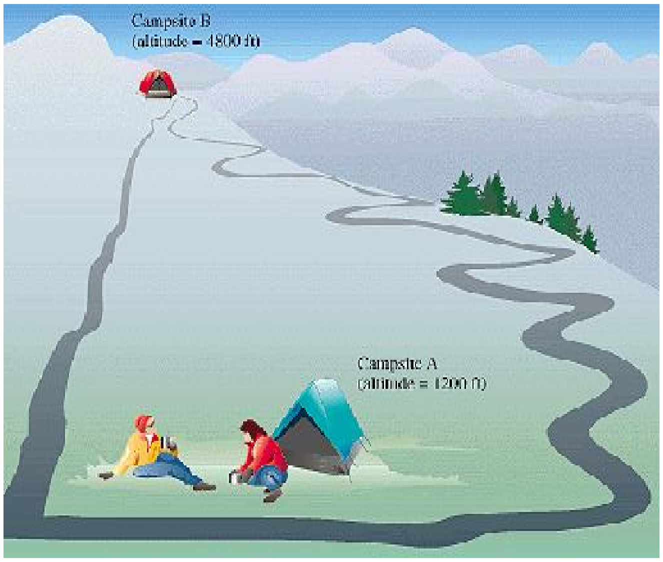
ENTHALPY AND ENTHALPY CHANGE

- **Enthalpy is an extensive property of a substance that can be used to obtain the heat absorbed or evolved in a chemical reaction.**
- (extensive property = property that depends on the amount of substance)

Symbol for Enthalpy: H

Enthalpy (H) is a State Function:

- **A State Function is a property of a system that depends only on its present state and independent of any previous history of the system**



Ex: Hiking in the mountains
You may take several alternative routes to reach certain peak

altitude reached
is analogous to a **state function**
(difference in altitude = 3600 ft)

distance traveled
is not analogous to **a state function**

ENTHALPY OF REACTION

Consider a chemical reaction: **REACTANTS** → PRODUCTS
At first: **Reactants only** No Products
The Enthalpy of the system = The Enthalpy of the Reactants =
H (reactants)

At the end: REACTANTS → **PRODUCTS**
No Reactants **Products only**
The Enthalpy of the system = The Enthalpy of the Products =
H (products)

The change in enthalpy = ΔH = Enthalpy of Reaction = H(products) - H(reactants)

The value of ΔH:
- is independent of the details of the reaction
- depends only on the initial state (reactants) and the final state (products)

Recall that H is a state function!

- THE ENTHALPY OF REACTION EQUALS THE HEAT OF REACTION AT CONSTANT PRESSURE:

$$\Delta H = q_p$$

where: ΔH = Enthalpy of reaction
q_p = Heat of reaction at constant pressure

THERMOCHEMICAL EQUATIONS

- In a thermochemical equation, the enthalpy of a reaction is indicated after the equation and is associated with the molar coefficients of the equation.

Example:

$2H_2(g)$	$+$	$O_2(g)$	$\longrightarrow$	$2H_2O\ (g)$		**$\Delta H = -483.7$ kJ**
2 mol of H_2 gas	reacts with	1 mole O_2	to produce	2 mol of **water vapor**	and	**483.7 kJ evolves**

NOTE: Indicating phase labels in thermochemical equations is very important

Consider:

$$2H_2(g) \quad + \quad O_2(g) \quad \longrightarrow \quad 2H_2O\ (l) \qquad \Delta H = -\ 571.7\ \text{kJ}$$

This equation says: 2 mol of hydrogen gas reacts with one mole of oxygen gas to produce 2 mole of **liquid** water, and **571.7 kJ** of heat evolves.
(additional heat is released when water vapor condenses to liquid)

MANIPULATING THERMOCHEMICAL EQUATIONS

1. Changing the coefficients of the balanced chemical equation, changes the **value** of **ΔH** accordingly

Example:
Liquid carbon disulfide burns in air, producing carbon dioxide gas and sulfur dioxide gas.

$$1\ CS_2(l) + 3\ O_2(g) \longrightarrow 1\ CO_2(g) + 2SO_2(g) \qquad \Delta H = -1075\ kJ$$

What is ΔH for the following equation ?

$$\tfrac{1}{2}\ CS_2(l) + 3/2\ O_2(g) \longrightarrow \tfrac{1}{2}\ CO_2(g) + 1\ SO_2(g) \qquad \Delta H = ?$$

Note: All the coefficients are halved

Therefore: $$\Delta H = -\frac{1075\ kJ}{2} = -537.5\ kJ$$

RULE 1

- **When a thermochemical equation is multiplied (or divided) by any factor, the value of ΔH for the new equation is obtained by multiplying(or dividing) the value of ΔH in the original equation by that same factor.**

2. **Reversing the thermochemical equation, changes the sign of ΔH accordingly**

Example:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H = -571.7\ kJ\ (exothermic)$$

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g) \qquad \Delta H = +571.7\ kJ\ (endothermic)$$

RULE 2

- **When a thermochemical equation is reversed, the value of ΔH is reversed in sign**

Examples:

1. With a platinum catalyst, ammonia gas will burn in oxygen gas to give gaseous nitrogen monoxide and water vapor:

$$4\ NH_3(g) + 5\ O_2(g) \longrightarrow 4\ NO(g) + 6\ H_2O(g) \qquad \Delta H = -906\ kJ$$

What is the enthalpy change for the following reaction?

$$NO(g) + 3/2\ H_2O(g) \longrightarrow NH_3(g) + 5/4\ O_2(g) \qquad \Delta H = ?$$

Step 1: First reverse the given equation:

$$4\ NO(g) + 6\ H_2O(g) \longrightarrow 4\ NH_3(g) + 5\ O_2(g) \qquad \Delta H = +906\ kJ$$

Step 2: Divide the coefficients and ΔH by 4:

$$NO(g) + 3/2\ H_2O(g) \longrightarrow NH_3(g) + 5/4\ O_2(g) \qquad \Delta H = +227\ kJ$$

APPLYING STOICHIOMETRY TO HEATS OF REACTION

2. Propane, C_3H_8, is a common fuel gas. Use the following to calculate the **grams of propane** you would need to provide **255 kJ of heat.**

$$\underset{?\ g}{C_3H_8} + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(g) \qquad \Delta H = -2044\ kJ$$

$$\Delta H = -255\ kJ$$

$$?\ g\ C_3H_8 = 255\ kJ \times \frac{1\ mol\ C_3H_8}{2044\ kJ} \times \frac{44.06\ g}{1\ mol\ C_3H_8} = 5.50\ g$$

HEAT CAPACITY AND SPECIFIC HEAT

HEAT CAPACITY , C

- The quantity of heat needed to raise the temperature of a sample of a substance one degree Celsius (or one degree Kelvin)

Recall : $K = {}^0C + 273$

NOTE: $\Delta K = \Delta\, {}^0C$

(Change in temperature in Kelvin) Change in temperature in ${}^0C$)

$q = C\, \Delta t$ where **q** = quantity of heat required to produce the temperature change

$\Delta t = t_f - t_i$ = change in temperature from an initial temp., t_i, to a final temp., t_f

C = Heat capacity

- **HEAT CAPACITY(C) is directly proportional to the mass of substance**
- **MOLAR HEAT CAPACITY** = Heat capacity for one mole of substance
- **SPECIFIC HEAT CAPACITY or SPECIFIC HEAT, s**
  Quantity of heat required to raise the temperature of one gram of substance by one degree Celsius (or one Kelvin) at constant pressure

$q = m \times s \times \Delta t$ where

m = mass
s = specific heat
Δt = temperature difference

Specific Heat and **Molar Heat Capacity**:

- are different for different substances
- are **physical constants, characteristic for a specific substance**
- are slightly temperature dependent (usually given at 25^0 C)
- are available in Tables in textbooks

$$\text{Specific Heat of water} = \boxed{1.00\ \frac{\text{cal}}{\text{g} \times {}^0\text{C}}} = \boxed{4.18\ \frac{\text{J}}{\text{g} \times {}^0\text{C}}}$$

Examples:

1. How much heat (in joules) must be used to raise the temperature of 185 g of water from 15 ^{0}C to 96 ^{0}C ?

$m = 185\ g$

$t_i\ = 15\ ^\circ C$

$t_f\ = 96\ ^\circ C$

$\Delta t = 96\ ^\circ C - 15\ ^\circ C = 81\ ^\circ C$

$$s = \ 4.18\ \frac{J}{g\ \ x\ ^\circ C}$$

q = ?

$$\mathbf{q = m\ \ x\ s\ x\ \Delta t}$$

$$q = (185\ g)\ (\ 4.18\ \frac{J}{g\ \ x\ ^\circ C})\ (\ 81^\circ C\ )$$

$q = 6.3\ x\ 10^4\ J =$ **63 kJ**

2. A sample of aluminum with a mass of 40.0 g requires 726 J of heat to raise its temperature from 30.0°C to 50.0 °C. What is the specific heat of aluminum?

3. What is the heat capacity of 25.0 g of ethyl alcohol if its specific heat is 2.42 J/g°C?

4. Molar heat capacity of iron is 25.1 J/mol°C. What is the specific heat of iron?

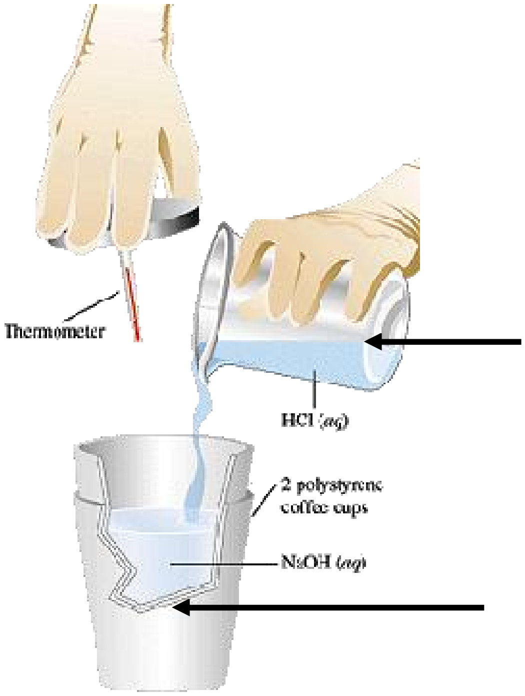
CALORIMETRY

- The experimental method for measurement of heat is called **calorimetry**.
- A calorimeter is a device used to measure the heat absorbed or evolved during a physical or chemical change.
- A calorimeter is an insulated container (styrofoam coffee cup or a Snack-Jar equipped with a thermometer.
- It is used to measure temperature changes which are then related to changes in heat energy.

Sample Problem 1:
50.0 mL each of 1.0 M HCl and 1.0 M NaOH, at room temperature (20.0 ^{O} C) are mixed. The temperature of the resulting NaCl solution increases to 27.5 ^{O} C.

The density of the resulting NaCl solution is 1.02 g/mL.
The specific heat of the resulting NaCl solution is 4.06 J/g ^{0} C

Calculate the **Heat of Neutralization of HCl(aq) and NaOH(aq) in KJ/mol NaCl produced**



50.0 mL HCl, 1.0 M (20.0^{0}C)

50.0 mL NaOH, 1.0 M (20.0^{0}C)

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$ + Heat of Neutralization (ΔH)

Heat given off by the Neutralization Rxn = Heat gained by the NaCl solution

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$ **ΔH = ???**

ΔH = exothermic (temperature of solution increased)

mass of solution: V x d = (100.0 mL) x (1.02 g/mL) = 102 g
m = 102 g
Specific heat = 4.06 J/g °C
Δt = 7.5 °C

q = **– m x s x Δt**

ΔH = – (102 g) (4.06 J/g °C) (7.5 °C) = –3100 J = **–3.1 kJ (exothermic reaction)**

$$\frac{-3.1\text{ kJ}}{\text{mol of NaCl produced}} = ?$$

mol NaCl produced = ?

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

HCl(aq)	NaOH(aq)	NaCl(aq)
50.0 mL	**50.0 mL**	**? mol**
1.0 M	**1.0 M**	

NOTE: Reactants are in stoichiometric ratio (No Limiting Reactant, No Reactant in excess)

Therefore: The resulting moles of NaCl can be calculated from the volumes of either NaOH solution or HCl solution.

$$? \text{ mol NaCl} = 50.0\text{mL HCl} \times \frac{1.0 \text{ mol HCl}}{1000 \text{ mL HCl}} \times \frac{1 \text{ mol NaCl}}{1 \text{ mol HCl}} = \mathbf{0.0050 \text{ mol NaCl}}$$

$$\Delta H = - \frac{-3.1 \text{ KJ}}{0.050 \text{ mol NaCl produced}} = \mathbf{- 62 \text{ KJ/mol}}$$

Sample Problem 2:

2.08 g of NaOH are dissolved in 50.0 mL of water whose temperature is 20.0 °C. The temperature of the NaOH solution after mixing increases to 28.8 °C.

The specific heat of the resulting NaOH solution is about 3.93 J/g °C

Calculate the Heat of Solution of NaOH in KJ/mol

$$\underset{2.08\ \text{g}}{\mathbf{NaOH(s)}} \quad + \quad \underset{50.0\ \text{g}}{\mathbf{H_2O(l)}} \quad \longrightarrow \quad \underset{52.1\ \text{g}}{\mathbf{NaOH(aq)}} \qquad \Delta H = ???$$

Heat of solution of NaOH = ΔH = exothermic (temperature of solution increased)

Mass of solution = 52.1 g
Initial Temperature = 20.0 °C.
Final Temperature = 28.8 °C
Δt = 8.8 °C
Specific heat = 3.93 J/g °C

q = m x s x Δt

$q = -(52.1\ \text{g})(3.93\ \text{J/g °C})(8.8\ \text{°C}) = -1800\ \text{J} = \mathbf{-1.8\ KJ}$

$$?\ \text{mol NaOH} = 2.08\ \text{g}\ \frac{1\ \text{mol}}{40.0\ \text{g}} = \mathbf{0.052\ mol\ NaOH}$$

$$\textbf{Heat of solution} = \Delta H = ?\ \frac{\text{kJ}}{\text{mol NaOH}} \qquad \Delta H = \frac{-1.8\ \text{kJ}}{0.052\ \text{mol NaOH}} = \mathbf{-35\ KJ/mol}$$

Sample Problem 3:

0.562 g of graphite is placed in a calorimeter with excess oxygen at 25.00 °C and 1 atm pressure. The graphite is ignited and burns completely to form CO_2 as shown below:

$$C\ (\text{graphite}) + O_2 \rightarrow CO_2\ (g)$$

After the completion of the reaction, the calorimeter temperature rises to 25.90 °C. The heat capacity of the calorimeter is found to be 20.7 kJ/°C. Based on this information calculate the heat of the reaction.

Examples:

1. Two solutions, 100.0 mL of 1.00 M $AgNO_3$ and 100.0 mL of 1.00 M NaCl, both initially at 22.4 °C, are added to a calorimeter and allowed to react. The temperature rises to 30.2 °C. Calculate the heat of reaction in kJ/mol AgCl produced. (Assume density and specific heat of solution to be the same as water)

2. A 0.205-g pellet of potassium hydroxide, KOH, is dissolved in 56.0 g of water in a calorimeter. The water temperature rises from 23.5 to 24.4 °C. Calculate ΔH_{soln} in kJ/mol KOH. (Assume the specific heat of the solution to be the same as water, 4.184 J/g°C)

3. When 23.6 g of $CaCl_2$ was dissolved in water in a calorimeter, the temperature rose from 25.0°C to 38.7°C. If the heat capacity of the calorimeter and the solution is 1258 J/°C, what is the ΔH_{soln} for $CaCl_2$ in kJ/mol?

HESS'S LAW

Hess's Law of Summation

- **For a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation equals the sum of the enthalpy changes for the individual steps.**

Example:

Ammonia will burn in the presence of a platinum catalyst to produce nitric oxide, NO

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g) \qquad \Delta H = ?$$

What is the heat of reaction at constant pressure?

Use the following thermochemical equations:

$$N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta H_1 = +\ 180.6\text{ kJ (Eq 1)}$$

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H_2 = -\ 91.8\text{ kJ (Eq 2)}$$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \qquad \Delta H_3 = -\ 483.7\text{ kJ (Eq 3)}$$

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g) \qquad \Delta H = ?$$

- **Step 1:** To get 4 $NH_3(g)$ on the reactant side: **Multiply Eq 2 by 2,** and reverse its its direction:

$$N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta H_1 = +180.6\text{ kJ} \qquad \text{(Eq 1)}$$

$$4NH_3(g) \longrightarrow 2N_2(g) + 6H_2(g) \qquad \Delta H_2 = (\ -91.8\text{ kJ})\ (-2) = +184\text{ kJ (Eq 2)}$$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \qquad \Delta H_3 = -\ 483.7\text{ kJ} \qquad \text{(Eq 3)}$$

$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$ $\Delta H = ?$

- **Step 2**: To get 4 NO (g) on the product side: Multiply **Eq 1 by 2:**

$2N_2(g) + 2O_2(g) \longrightarrow 4NO(g)$ $\Delta H_1 = (+180.6\ kJ)(2) = +361.2\ kJ$ (Eq 1)

$4NH_3(g) \longrightarrow 2N_2(g) + 6H_2(g)$ $\Delta H_2 = +184\ kJ$ (Eq 2)

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$ $\Delta H_3 = -483.7\ kJ$ (Eq 3)

- **Step 3:** To get 6 H_2O (g) on the product side: **Multiply Eq 3 by 3:**

$2N_2(g) + 2O_2(g) \longrightarrow 4NO(g)$ $\Delta H_1 = +361.2\ kJ$ (Eq 1)

$4NH_3(g) \longrightarrow 2N_2(g) + 6H_2(g)$ $\Delta H_2 = +184\ kJ$ (Eq 2)

$6H_2(g) + 3O_2(g) \longrightarrow 6H_2O(g)$ $\Delta H_3 = -483.7\ kJ\ (3) = -1450\ kJ$ (Eq 3)

- **Step 4**: Add the 3 steps (equations) and cancel out $2N_2(g)$ and $6H_2(g)$

$\cancel{2N_2(g)} + 2O_2(g) \longrightarrow 4NO(g)$ $\Delta H_1 = +361.2\ kJ$ (Eq 1)

$4NH_3(g) \longrightarrow \cancel{2N_2(g)} + \cancel{6H_2(g)}$ $\Delta H_2 = +184\ kJ$(Eq 2)

$\cancel{6H_2(g)} + 3O_2(g) \longrightarrow 6H_2O(g)$ $\Delta H_3 = -1450\ kJ$ (Eq 3)

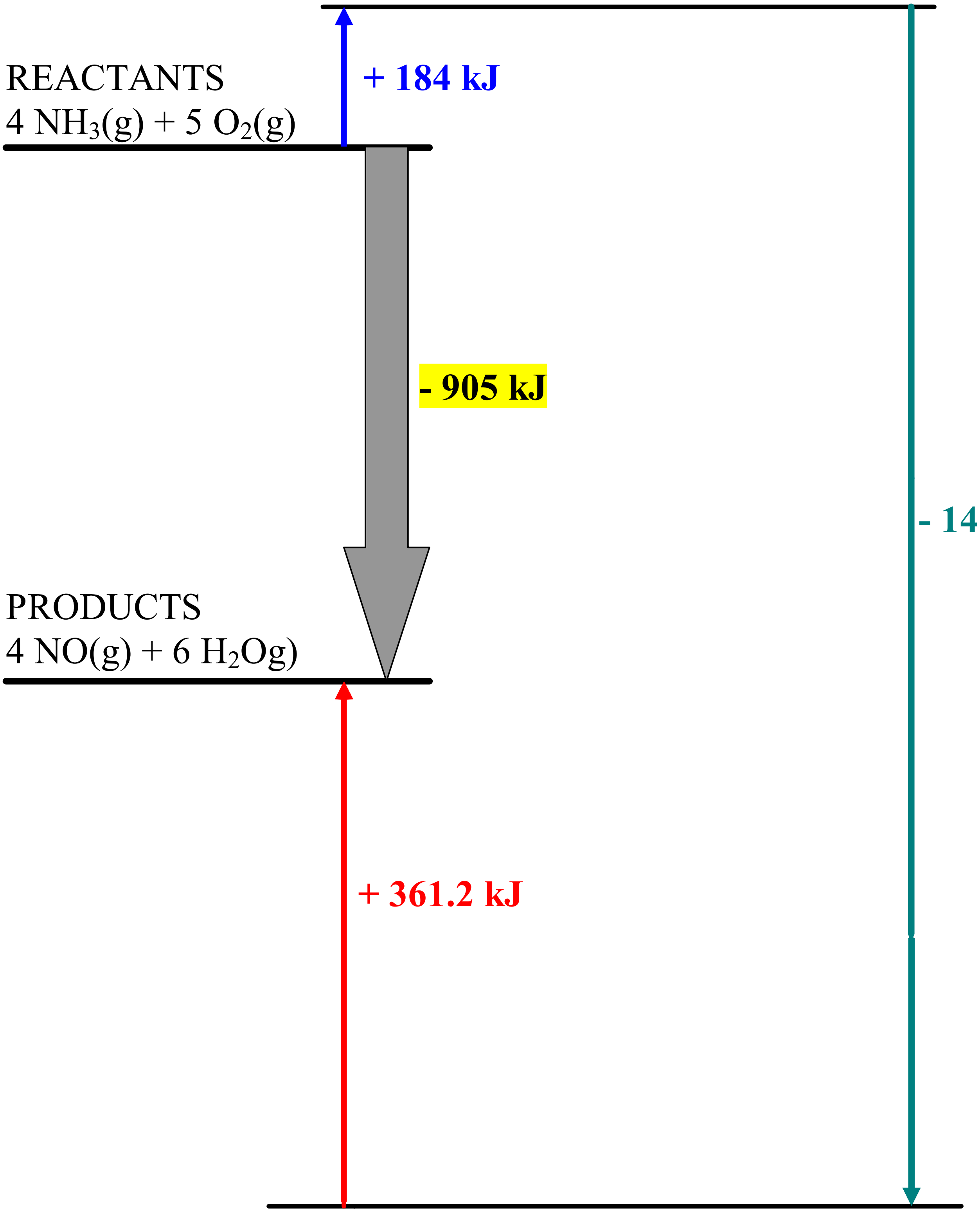
$2O_2(g) + 4NH_3(g) + 3O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$ $\Delta H_T = \Delta H_1 + \Delta H_2 + \Delta H_3$

$\Delta H_T = +361.2\ kJ + 184\ kJ - 1450\ kJ = -905\ kJ$

SUM:

$5O_2(g) + 4NH_3(g) \longrightarrow 4NO(g) + 6H_2O(g)$ $\Delta H_T = -905\ kJ$

- An Enthalpy diagram illustrating how Hess's law applies to this example is shown below.



Examples:

1. Calculate the enthalpy of reaction for the reaction shown below:

$C_2H_4\ (g) + H_2\ (g) \rightarrow C_2H_6\ (g)$ $\Delta H = ???$

from the following:

$C_2H_4\ (g) + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 2\ H_2O\ (l)$ $\Delta H = -1401$ kJ

$2\ C_2H_6\ (g) + 7\ O_2\ (g) \rightarrow 4\ CO_2\ (g) + 6\ H_2O\ (l)$ $\Delta H = -3100$ kJ

$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (l)$ $\Delta H = -572$

2. Calculate the enthalpy of reaction for the reaction shown below:

$CH_4\ (g) + NH_3\ (g) \rightarrow HCN\ (g) + 3\ H_2\ (g)$

from the following equations:

$N_2\ (g) + 3\ H_2\ (g) \rightarrow 2\ NH_3\ (g)$ $\Delta H = -91.8$ kJ

$C(graphite) + 2\ H_2\ (g) \rightarrow CH_4\ (g)$ $\Delta H = -74.9$ kJ

$H_2\ (g) + 2\ C(graphite) + N_2\ (g) \rightarrow 2\ HCN\ (g)$ $\Delta H = 270.3$ kJ

STANDARD ENTHALPIES OF FORMATION

Standard State = **Standard Thermodynamic Conditions**

Indicated by a superscript: (^{o})

(1 atm pressure and 25^o C)

Standard Enthalpy of Reaction, ΔH^o (Read delta H zero)

- The Enthalpy change for a reaction in which reactants in their standard states yield products in their standard state.

- Tables usually give Enthalpy changes for **Formation Reactions** only.

Formation Reactions:

Reactions in which compounds are formed from their elements

$$A + B \longrightarrow AB$$

Example:

$$C(graphite) + 2Cl_2(g) \longrightarrow CCl_4(l) \qquad \Delta H^o_f = -139 \text{ kJ/mol}$$

- Standard Enthalpy of formation for liquid CCl_4 from graphite = 139 kJ/mol

Note:

- It is important to indicate the form in which the element participates in a formation reaction, since the value of ΔH^o_f is determined by this.

- Carbon may exist in other forms as well, referred to as allotropes (ex: diamond).

- However, graphite is the most stable form of carbon (Graphite is referred to as the reference form of carbon)

Reference form of an element :

- The most stable form of the element under standard thermodynamic conditions (1 atm pressure and 25° C)

ΔH^o_f of an element in its reference form = 0

For example:

ΔH^o_f (graphite) = 0
ΔH^o_f (diamond) = 1.9 kJ/mol

Meaning:

$$C(\text{graphite}) \longrightarrow C(\text{diamond}) \qquad \Delta H^o_f = +1.9 \text{ kJ/mol (endothermic)}$$

ΔH^o_f = STANDARD ENTHALPY OF FORMATION
= STANDARD HEAT OF FORMATION
= is the enthalpy change for the formation of one mole of the substance in its standard state from its elements in their reference form and in their standard states.
(For Values, see Table 6.2, and in Appendix C)

Applications:

- Using Hess's Law, the given standard enthalpies of formation can be used to find the standard enthalpy change for a reaction.

Examples:

1. The cooling effect of alcohol on the skin is due to its evaporation. Calculate **the heat of vaporization of ethanol** (ethyl alcohol), C_2H_5OH.

$$C_2H_5OH\ (l) \longrightarrow C_2H_5OH\ (g) \qquad \Delta H^o \text{ vaporization} = ?$$

From Table 6.2 or Appendix C:

$\Delta H^o_f[C_2H_5OH(l)] = -277.6$ kJ/mol

$\Delta H^o_f[C_2H_5OH(g)] = -235.4$ kJ/mol

$$\begin{array}{llcll} & C_2H_5OH(l) & \longrightarrow & C_2H_5OH(g) & \Delta H^o \text{ vaporization} = ? \\ \Delta H^o_f & -277.6 \text{ kJ/mol} & & -235.4 \text{ kJ/mol} & \end{array}$$

ΔH^o vaporization = $\Delta H^o_f[C_2H_5OH(g)] - \Delta H^o_f[C_2H_5OH(l)]$

ΔH^o vaporization = (-235.4 kJ/mol) - (-277 kJ/mol) = **+ 42. 2 kJ/mol**

Note: Positive sign indicates that reaction is endothermic

- **IN GENERAL, ΔH^o for a reaction can be calculated as:**

ΔH^o = Sum of ΔH^o_f of products – Sum of ΔH^o_f of reactants

$\Delta H^o = \Sigma\, n\, \Delta H^o_f\,(\text{products}) - \Sigma\, m\, \Delta H^o_f\,(\text{reactants})$

where: Σ = mathematical symbol for "the sum of"
n, m, = the coefficients of the substances in the chemical equation

Examples:

2. Iron is obtained from iron ore by reduction with carbon monoxide. The overall reaction is shown below. Calculate the standard enthalpy change for this equation. See Appendix C for ΔH°_f data.

	Fe_2O_3 (s)	+	3 CO (g)	$\longrightarrow$	2 Fe (s)	+	3 CO_2 (g)
ΔH^o_f (kJ/mol)	–825.5		–110.5		0		–393.5

$\Delta H^o = \Sigma\, n\, \Delta H^o_f\,(\text{products}) - \Sigma\, m\, \Delta H^o_f\,(\text{reactants})$

= [2 (0) + 3 (–395.5)] – [(–825.5) + 3 (–110.5) = –23.5 kJ

3. Calculate the standard enthalpy of formation for ethylene (C_2H_2) from the standard enthalpies of reaction shown below:

	2 C_2H_2 (g) +	5 O_2 (g) →	4 CO_2 (g) +	2 H_2O (g)	ΔH° = –2512 kJ
$\Delta H_f\,^\circ$ (kJ/mol)	??	0	–393.5	–242	